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14. ABSTRACT

We report a systematic investigation of the morphology of sulfonated styrenic pentablock copolymer solutions and membranes obtained from Kraton Polymers LLC. The polymer studied was poly((t-butyl-styrene)-b-(ethylene-r-butylene)-b-(styrene-r-styrene sulfonate)-b-(ethylene-r-butylene)-b-(t-butyl-styrene)). Small angle x-ray scattering (SAXS) revealed that the solutions exhibited micellar morphologies. The solution SAXS data was modeled using the Kinning-Thomas model to obtain radius of the micelle core, the radius of closest approach between two micelles and the number density of micelles; these characteristics will be correlated to suspension viscosity to aid in membrane production. The membranes have microphase

15. SUBJECT TERMS

block copolymer, morphology, pentablock, sulfonate polystyrene

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Report Title

Improved Chem/Bio Protection Clothing for Military Personnel by Probing Nanoscale Structure in Block Copolymers

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List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Number of Papers published in peer-reviewed journals: 0.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

MORPHOLOGY OF SULFONATED STYRENIC PENTABLOCK COPOLYMER SOLUTIONS AND MEMBRANES, by Arun Kota and Karen I. Winey; accepted for the March Meeting of the American Physical Society Meeting, Pittsburg, PA, scheduled for March 2009.

Number of Presentations: 1.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

MORPHOLOGY OF SULFONATED STYRENIC PENTABLOCK COPOLYMER SOLUTIONS AND MEMBRANES, by Arun Kota and Karen I. Winey; accepted for Annual Technical Meeting of the Society of Plastics Engineering, Chicago, IL, scheduled for June 2009.

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 1

(d) Manuscripts

Number of Manuscripts: 0.00

Number of Inventions:

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Arun Kota	1.00
FTE Equivalent:	**1.00**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Karen I. Winey	0.00	No
FTE Equivalent:	**0.00**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Improved Chem/Bio Protection Clothing for Military Personnel by Probing Nanoscale Structure in Block Copolymers

U.S. Army Research Office (8/15/07 to 7/14/08)
K. I. Winey (PI)

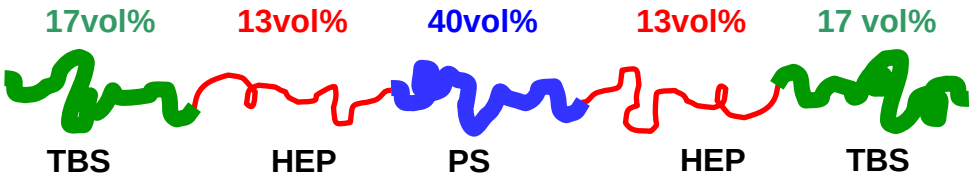
1. Statement of the Problem

Kraton Polymers has recently introduced a new block copolymer that contains a sulfonated polystyrene block. These materials have been designed and have demonstrated remarkable transport properties that are of considerable interest to the U.S. Army for chem/bio protective clothing. Our goal was to provide morphological characterization of these new materials to facilitate their production into membranes and to provide structure-property correlations.

Our works involves two aspects. We characterize pentablock suspensions, which have micellar morphologies, as a function of wt% solids, various solvents, and level of sulfonation. Here our work is providing both quality control of the suspensions and correlations with suspension viscosity to optimize membrane production. The characterization of the pentablock membranes is aimed at identifying the block copolymer morphology to provide a fundamental understanding of the structure-property relationships in these materials. Dr. Nathan Schneider has neutralized these membranes with metal cations to further enhance their potential for applications in chem/bio protection and our morphological studies have readily extended to these materials.

2. Summary of the Most Important Results

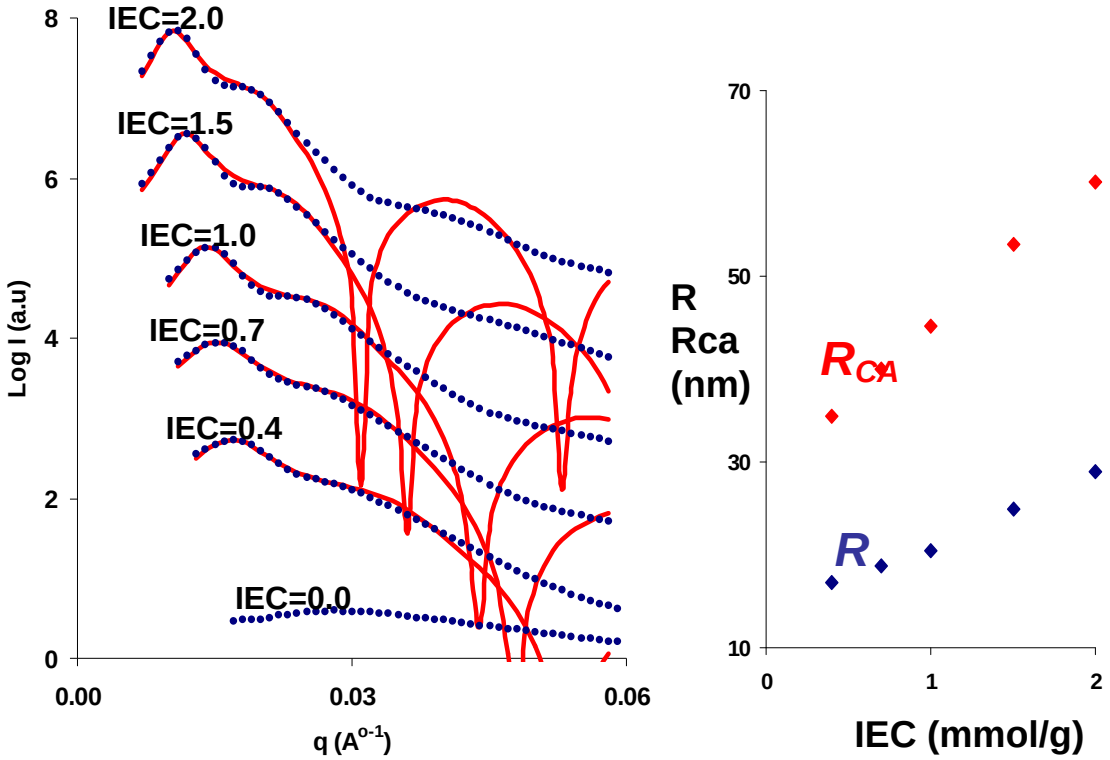
Pentablock Copolymers: The following pentablock copolymer has been synthesized by Kraton Polymers of Houston, TX. The midblock of this pentablock copolymer was subsequently sulfonated such that the ion exchange contents (IEC) are 0.4 to 2.0 mmol/g. These novel materials are now being commercialized by Kraton Polymers.



TBS	**–**	**Poly(*tert.* butyl styrene)**
HEP	**–**	**Hydrogenated Poly(ethylene-*co*-propylene)**
PS	**–**	**Polystyrene**

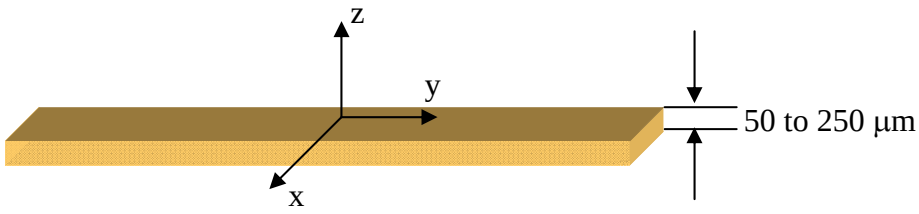
Pentablock Copolymer Suspensions: To facilitate the preparation of films, suspensions of pentablock copolymers are prepared in mixed solvent, wherein one of the solvents is typically cyclohexane. Film casting requires careful control of viscosity and is

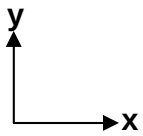
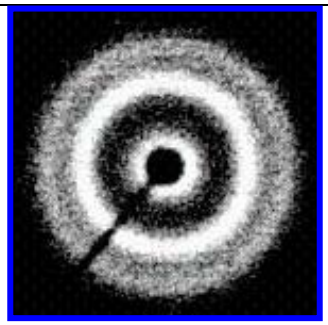
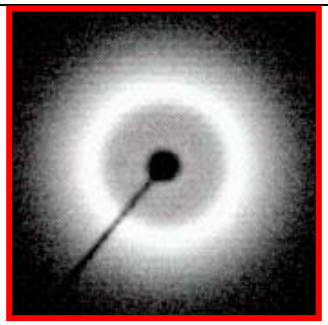
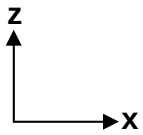
further enhanced by increasing the percent solids. X-ray scattering of these solutions reveals the expected micellar morphology (left figure; data – black dots). The Kinning-Thomas model was used to fit the data (left figure; model – red lines) and provides a measure the micelle size (right figure; R – core, Rca – core and corona) and the number density of aggregates. The values for R and Rca are found to increase significantly with IEC. This is accompanied by a decrease in the number of micelles per unit volume. We understand this finding by noting that as the level of sulfonation increases (IEC increasing) the interactions between the sulfonated polystyrene core and the endblocks and solvents become more unfavorable. These unfavorable interactions stretch the pentablock chains to minimize contact with area per junction point in the micelles. Stretching the pentablock copolymer also increases R and Rca as the level of sulfonation increases.



Pentablock Copolymer Membranes: X-ray scattering data show that the unsulfonated pentablock copolymers (IEC = 0 mmol/g) have a well-ordered microphase separated morphology. There are three well-defined scattering peaks, but the peak ratios do not readily correspond to any of the typical diblock copolymer morphologies. Upon sulfonation (IEC = 0.4 to 1.0 mmol/g), the first scattering peak becomes broader and the higher order reflections are lost. Thus, we conclude that sulfonation disturbs, but does not destroy the microphase separated morphology in the pentablock copolymer. Furthermore, the position of the first scattering peak remains constant indicating that the periodicity of the morphology is independent of sulfonation level.

When block copolymers are solvent cast into films, the microphase separated morphology is often anisotropic. For example, lamellae-forming diblock copolymers typically have anisotropic diffraction patterns when the X-rays are directed toward the sample in an edge-on orientation and signify that the lamellae preferentially lie in the plane of the film. In these pentablock copolymers, the anisotropic scattering patterns collected in the edge-on orientation are quite intriguing showing both peak intensity variations as a function of azimuthal angle and the maximum in the scattering vector changes. In other words, the edge on scattering pattern is a spotty oval rather than the more typical spotty circle. The oval scattering pattern means that the periodicity of the microphase separate morphology differs in the plan and through the plan. Specifically, in the plane the first scattering peak corresponds to ~ 29 nm (along the x and y directions) and through the plan the periodicity is only ~ 21 nm (along the z axis). This intriguing morphology is under further investigation.



Through Plane Scattering 			Isotropic diffraction pattern
Edge-on Scattering 			Anisotropic diffraction pattern
	IEC = 0 mmol/g	IEC = 1.0 mmol/g	